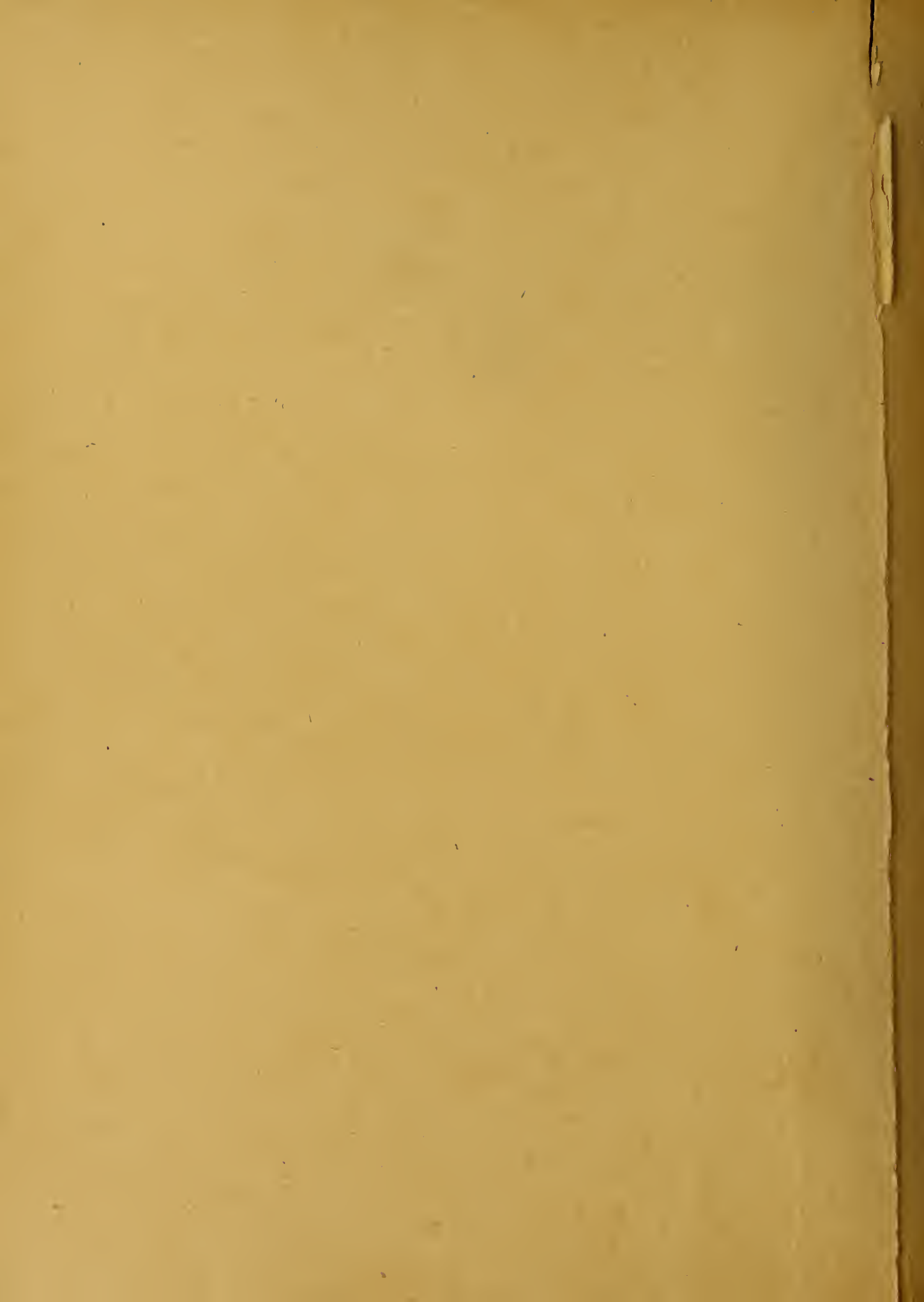


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Schneider - Emulsification of water gas tar for use



THE EMULSIFICATION OF WATER GAS TAR
FOR USE AS A DUST PREVENTIVE

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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THE EMULSIFICATION OF WATER GAS TAR
FOR USE AS A DUST PREVENTIVE

Introduction

The greatest developement in the preparation of dust preventives has been made in the utilization of bituminous products, such as petroleum oils, coal tar, coke oven tar, and water gas tar.

Petroleum oils, as a rule, penetrate much better than tar, but their true value is in the asphaltic base, and before maximum binding power is reached, the more volatile constituents of the oils must evaporate which is a slow process. In places where traffic is light, i.e. country roads, the lighter asphaltic and petroleum oils have been used. Although these oils are efficient road binders, they are not very permanent - at least two applications being necessary during the summer months in order to keep the roads in good condition.

Tars have been used to some extent as dust preventives and road binders, but not as much as the petroleum and asphaltic oils. The main objection to the use of tar is their viscosities which retards penetration to a great extent. Tar, for a few days after its application, is a nuisance on the roads and results in the damaging of personal property. Free carbon, ammonia, and naphthalene present in the tar are detrimental to its binding qualities. The light oils present are, however, valuable as diluents,

aiding in the penetration and later evaporating. The creosote oils prevent the tar from becoming too brittle, while the pitch represents the true binding value.

Experiments have shown that crude coal tar is not adapted to the treatment of roads as it does not amalgamate itself with the dust particles.* Coal tar results from the destructive distillation of coal and since this distillation is carried out at high temperatures, considerable free carbon is present as a result of the decomposition of hydrocarbons.

Coke oven tar is a product obtained in the treatment of gases from the manufacture of coke. Coal and coke oven tars have greater application in the dye and other chemical industries.

Water gas tar results chiefly from the cracking of petroleum oils used in enriching water gas for illuminating purposes. It is of little commercial importance except that it has been used to some extent as a road binder, and, when fluxed with pitch, forms a suitable roofing material that is quite impervious to water. For road purposes the crude is treated to remove the water and in so doing, a small percentage of the light oils is lost. The refined tar sells for 3-4 cents per gallon, while the crude sells for $1\frac{1}{2}$ cents per gallon.

Tar Emulsions

In 1903 and 1904 the use of oil emulsions for road treatment was introduced in France and Germany.** These emulsions contained an emulsifying agent, tar, and oil; tar giving the bind-

* Skinner, Am. Gas Light Jour. 92, 257-66.

** Hubbard, Dust Preventives and Road Binders.

ing qualities and the oil increasing the penetrating power. They were sold in a concentrated form which could be mixed with a considerable quantity of water and then applied to the road. It was hoped that these emulsions would prove to be efficient and permanent dust binders, but no data can be found relative to their success.

In Baltimore, Maryland after several years experience, it was found that emulsions as dust preventives were efficient and economical.* These emulsions consisted of a mixture of common rosin soap, oil, and tar; emulsified in a form that could be mixed with a considerable quantity of water before applying.

An emulsion is the product obtained by any process where two immiscible liquids are caused to disperse throughout each other. One phase is composed of a great number of individual particles which are separated from each other. This is known as the "dispersed phase". The second phase is usually continuous and lies between the particles of the first phase - this is known as the "dispersion means".**

C. R. Marshall in his paper on the "theory of emulsification" *** states that emulsification is a phenomenon of surface tension and that a third substance is necessary to produce a stable emulsion. He gives the following types of emulsifying agents:

* J. L. Wickes, Proc. Am. Soc. C. E. 37, 343.

** W. O. Ostwald, Koll. Zeit. 1, 291 (1907)

*** Pharm. Jour. 82, 257.

1. Colloidal substances soluble in water

- (a) Mucilaginous
- (b) Albuminous
- (c) Gelatinous

2. Alkalies

3. Saponins (and other preparations of vegetable drugs)

The literature contains numerous articles on the emulsification of tar, but information regarding the practical application of these emulsions is limited and the field presents great possibilities.

Purpose of investigation

The purpose of this thesis is; (1) to discuss the work previously done in this Laboratory on emulsions of water gas tar; (2) to discuss the relative merits of water gas tar as compared with other tars as a road material; (3) to study the properties of various types of emulsions; and (4) to study the practical application of these emulsions.

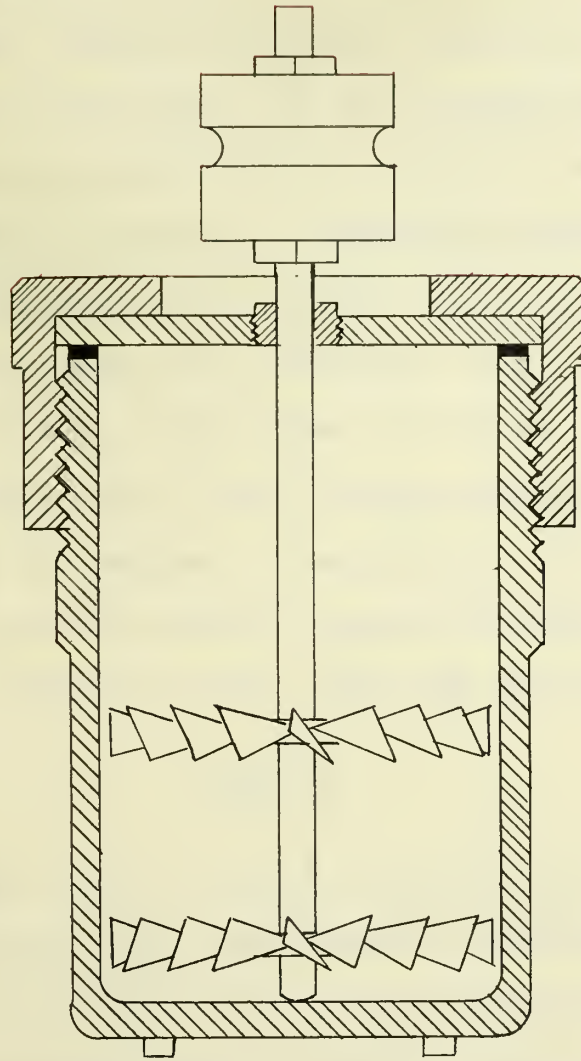


Fig. I

Experimental

Part I

The apparatus (Fig. I) used in this investigation consisted of a steel oxygen bomb having a 350 c.c. capacity. This particular type of apparatus was used largely because it was convenient. The two paddle wheels on the rod were so arranged that the liquids could be whirled in opposite directions, thus insuring an efficient agitation. The emulsion mixtures were introduced into the apparatus which was connected with a motor making an average speed of 2000 revolutions per minute. A small amount of heat was generated due to the friction between the sides of the oxygen bomb and the paddles of the stirrer, but in no case did the temperature of the mixtures exceed 40 degrees centigrade. All emulsions were stirred at this speed for 30 minutes.

Part II

In 1916, Rufus M. Kamm* experimenting in this Laboratory on emulsions of water gas tar, prepared emulsions of the following series: (a) tar-water; (b) sodium oleate-tar-water; (c) tar-sodium hydroxide-water; and (d) calcium chloride-tar-water. These emulsions were examined by the writer for stability having stood for twenty months. During this time the emulsions were not disturbed to any great extent, thus allowing the best conditions under which to settle. In no cases did these mixtures form stable emulsions. Kamm also prepared a series of sodium resinate-tar-

* Rufus M. Kamm, Thesis, Univ. of Ill. 1916.

water emulsions in which the emulsions containing 0.01% and 0.005% sodium resinate showed but slight separation. The comparative stability of these emulsions led the writer to make further investigation so as to ascertain the possibility of producing a stable mixture of this series. The following series of emulsions was prepared.

Table I

<u>No.</u>	<u>Concentration of rosin</u>	<u>% water</u>	<u>Character of emulsion</u>	<u>Time of separation</u>
1.	0.1	40	thin-streaky	2 days
2.	0.5	40	" "	2½ days
3.	1.0	40	oily-smooth	4 days
4.	2.0	40	oily-very smooth	no separation 90 days
5.	4.0	40	smooth	ditto
6.	5.0	40	smooth-thick	"
7.	10.0	40	smooth-viscous	"

The mixtures were introduced into the apparatus (Fig. I) and emulsified according to the directions as given on page 6. The sodium resinate and tar were first emulsified and the resultant product, a smooth viscous mass, was again emulsified with the water. It was found that a very stable emulsion could be prepared in this manner. As seen from the above table the best emulsion was prepared with a 2% concentration of sodium resinate. Increased rosin content caused an increase in this viscosity of the emulsion mixtures. Although the emulsions containing more than 2% sodium resinate were very stable, their viscosities would not permit a cold application. Heating the emulsions caused foaming, due to the relative large amounts of water.

Part III

The following analyses were made in an attempt to ascertain which tar was best suited for emulsification purposes.

Table II

Sample No.	1.	2.	3.	4.	5.	6.
Name of tar	Refined water gas	Refined water gas	Crude water gas	Crude water gas	Crude coal	Crude coke oven
Character of tar	mobile liquid	viscous liquid	thin mobile liquid	thin oily liquid	viscous liquid	viscous liquid
Specific Gr. 25 degrees C.	1.137	1.172	1.042	1.041	1.121	1.162
Free Carbon %	3.8	2.0	1.65	1.60	15.2	6.7
Bitumen sol. in C ₂ S %	96.1	97.5	98.2	97.6	84.4	93.1
Ash %	0.1	0.5	0.0	0.4	0.4	0.1
% water by volume	1.0	0.0	2.4	2.4	4.0	2.0
% 1st light oils 0-110 de. C.	1.0	0.6	3.6	3.5	2.5	2.8
% 2nd light oils 110-170 de. C.	0.8	2.5	17.5	18.1	17.5	15.9
% Heavy oils 170-270 De.C.	35.2	26.2	40.1	42.0	17.0	31.5
% Pitch residue 270 and up	62.0	70.2	36.4	34.0	59.0	47.8

Samples Nos. 1 and 3 were furnished by the Champaign, Urbana Gas and Electric Comapny, Champaign, Illinois. Samples Nos. 2, 4, 6, and 5 were obtained from the Illinois State Highway

Laboratory, Springfield, Illinois.

On cooling the second light oil fraction from the distillation of water gas tar, only a small amount of naphthalene precipitated out, while the heavy oil fraction showed no naphthalene. On cooling the same fraction from the coal and coke oven tar distillates, considerable quantities of naphthalene were found to be present.

From the above table of analyses, it can be plainly seen that refined water gas tar bears all the characteristic of a good road binder (see page 1) and should, therefore, make a suitable material for emulsification purposes. Its free carbon content is considerably lower than those of the other tars and it contains practically no ammoniacal liquors, as shown by the water fraction. The heavy oils fraction shows that a larger percent of creosote oils are present in the water gas tar than in the other tars, thus preventing the tar from becoming too brittle after the more volatile constituents of the tar have evaporated. The pitch residue is relatively higher than that of the other tars and for that reason should have a greater binding power.

Part IV

Sodium silicate ($\text{Na}_2\text{Si}_4\text{O}_9$), commonly called water glass has been used to some extent as a dust binder.* On account of its gelatinous and alkaline nature, it forms with water gas tar a very stable emulsion. Water glass on exposure to the air absorbs carbon dioxide and gelatinous silicic acid is precipitated

* Hubbard, Dust Preventives and Road Binders

acts as a temporary binder for the small dust particles on the road. The following table will show some of the characteristics of water glass-tar emulsions.

Table III

<u>No.</u>	<u>% water</u>	<u>% Sodium silicate</u>	<u>Character of Emulsion</u>	<u>Time of Separation</u>
1.	30	0.5	thin-streaky	24 hours
2.	"	1.0	" "	30 "
3.	"	4.0	Smooth	slight separation after 6 days
4.	"	5.0	" oily	no visible separation after 2 months
5.	"	10.0	granular-viscous	no separation after 3 months
6.	"	15.0	viscous-granular	ditto

The best emulsion was obtained with a 5% concentration of sodium silicate-the specific gravity of the sodium silicate solution being the same as that of the tar. The viscosity of the emulsions increased with an increase in the concentration of sodium silicate (Sp. Gr. 1.38), and those emulsions containing more than 5% sodium silicate could not be applied to the road in a cold condition.

It was found that on the addition of calcium chloride, the insoluble colloidal calcium silicate was precipitated which acts as a binding medium for the dust particles. Also, the colloidal nature of the calcium silicate aids materially in forming a stable emulsion. A series of sodium silicate-calcium chloride-tar and water emulsions was prepared and the following table gives some of the characteristics of these emulsions.

Table IV

<u>No.</u>	<u>% Water</u>	<u>% Sodium silicate</u>	<u>% Calcium chloride</u>	<u>Character of emulsion</u>	<u>Time of separation</u>
1.	40	0.1	0.5	streaky	6 hours
2.	"	0.5	1.0	thin-streaky	4 hours
3.	"	1.0	2.0	thin-smooth	2½ days
4.	"	2.0	4.0	smooth	48 hours
5.	"	2.5	5.0	smooth-oily	4 days
6.	"	3.0	10.0	very smooth-oily	no separation
7.	"	5.0	10.0	smooth-semi-viscous	2 months ditto
8.	"	10.0	15.0	granular-viscous	ditto

The addition of calcium chloride in excess serves a dual purpose. Calcium chloride solutions* have been used to some extent for dust laying purposes but frequent rains wash away the salt and repeated applications are expensive. It has already been mentioned that calcium chloride reacts with sodium silicate to form colloidal calcium silicate which acts as a temporary binder. Microscopic examinations show the calcium chloride present in the dispersed phase. The tar and colloidal silicate act as an envelope to protect the calcium chloride crystals from being washed out.

In order to test the binding qualities of the above emulsions, small test boxes were prepared which consisted of a small wooden box (2"x5"x8") filled two thirds full with earth taken from the crest of an ordinary loamy road. The emulsions were applied cold to these test boxes and exposed to climatic conditions for a period of two weeks, and in every case excellent

* Hubbard, Dust Preventives and Road Binders.

binding qualities were exhibited.

It has been demonstrated that a stable emulsion of tar and water, although theorectically possible, cannot actually be prepared.* Marshall has shown that the additon of a third substance or emulsifying agent is necessaryto produce a stable emulsion.** From the foregoing experiments it will be seen that it is not an impracticable possibility to prepare a stable emulsion of tar and water, with the addition of a third substance, that will serve in every capacity as a dust preventive and road binder.

* Bancroft, Jour. Phys. Chem. 16, 233 (1910)

** Pharm. Jour. 82, 257

SUMMARY

The results of this investigation briefly summarized are:-

(1). It is possible to prepare a very stable emulsion of sodium resinate, tar, and water; by emulsifying the first two constituents and later adding the water.

(2). Water gas tar bears all the characteristics of a good road binder and should, therefore, be suitable and cheap material for emulsification purposes.

(3). A very stable emulsion of sodium silicate, (water glass) tar, and water can easily be prepared.

(4). The stability of the emulsions is dependent largely on the specific gravity of the emulsifying agent.

(5). The addition of calcium chloride to water glass emulsions increases the stability of these emulsions and adds to their binding powers.

(6). Microscopic examinations show that the tar and sodium silicate form an envelope for the calcium chloride particles, thus preventing the calcium chloride from being washed away.

(7). Emulsions of water gas tar are not an impractical possibility.

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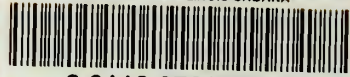
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